CLIPPEDIMAGE= JP411340090A

PAT-NO: JP411340090A

DOCUMENT-IDENTIFIER: JP 11340090 A

TITLE: MANUFACTURE OF GRAIN BOUNDARY INSULATED MULTILAYER CERAMIC CAPACITOR

PUBN-DATE: December 10, 1999

INVENTOR-INFORMATION:

NAME	COUNTRY
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INT-CL (IPC): H01G004/30

ABSTRACT:

PROBLEM TO BE SOLVED: To provide a grain boundary insulated multilayer ceramic
capacitor exhibiting a high moisture resistance.

SOLUTION: The surface of a sintered compact of grain boundary insulating type
multilayer ceramic capacitor containing strontium and barium titanate as major
component is coated with glass paste exhibiting a lower melting point than the
reoxidation temperature of the sintered compact. Then baking and diffusion is
performed to form a glass diffused layer 4 on the surface of the sintered
compact. In this way, many pores in the surface part of the sintered compact
are filled with glass through the baking and diffusion of glass in order to
prevent the moisture from penetrating to the inside of the sintered compact
even in a high humidity atmosphere and to prevent degradation of
characteristics.

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Abstract - FPAR:

SOLUTION: The surface of a sintered compact of grain boundary insulating type multilayer ceramic capacitor containing strontium and barium titanate as major component is coated with glass paste exhibiting a lower melting point than the reoxidation temperature of the sintered compact. Then baking and diffusion is performed to form a glass diffused layer 4 on the surface of the sintered compact. In this way, many pores in the surface part of the sintered compact are filled with glass through the baking and diffusion of glass in order to prevent the moisture from penetrating to the inside of the sintered compact even in a high humidity atmosphere and to prevent degradation of characteristics.

(19)日本国特許庁（JP）　(12)公開特許公報（A）　(11)特許出願公開番号

特開平11－340090

(43)公開日　平成11年(1999)12月10日

(51)Int.Cl.[6]	識別記号	FI	
H01G 4/30	311	H01G 4/30	311Z

審査請求　未請求　請求項の数4　OL　（全 5 頁）

(21)出願番号　特願平10－148970

(22)出願日　平成10年(1998)5月29日

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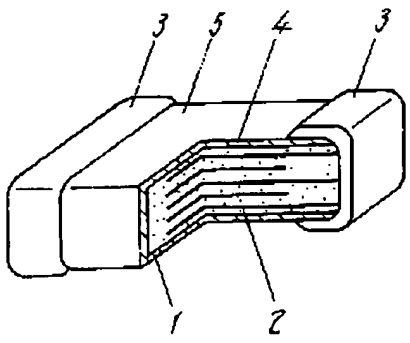
(54)【発明の名称】　粒界絶縁型積層セラミックコンデンサの製造方法

(57)【要約】
【課題】　耐湿特性の優れた粒界絶縁型積層セラミックコンデンサを提供することを目的とする。
【解決手段】　チタン酸ストロンチウム、バリウムを主成分とする粒界絶縁型積層セラミックコンデンサの焼結体表面に、前記焼結体の再酸化処理温度より低い融点を有するガラスペーストを塗布し、焼付け拡散処理を行いガラス拡散層4を焼結体表層部に形成する。

1 積層体
2 内部電極
3 外部電極
4 ガラス拡散層
5 オーバーコート膜



91
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1 積層体
2 内部電極
3 外部電極

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＊4 ガラス拡散層
5 オーバーコート膜
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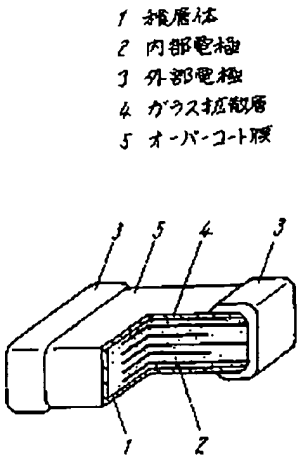
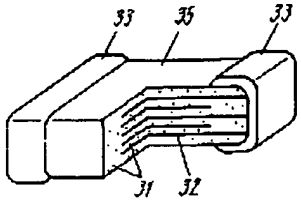
【図１】



【図２】



* NOTICES *

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2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the grain-boundary insulation type laminating ceramic condenser characterized by applying the glass paste characterized by providing the following, and performing printing diffusion process of glass. The dielectric layer which makes strontium-titanate barium a principal component. It is the melting point lower than reoxidation processing temperature after carry out two or more layer laminating of the internal electrode by turns, obtaining a layered product, carrying out the laminating of the above-mentioned internal electrode so that it may pull out at the edge at which this layered product conflicts on both sides of the above-mentioned dielectric layer by turns and the section may be exposed to it, calcinating this layered product and obtaining a sintered compact to this sintering body surface.

[Claim 2] After applying external electrode paste to the ends side of the sintered compact which the drawer section of an internal electrode exposed so that it may connect with the above-mentioned internal electrode electrically, The glass paste which has the melting point lower than reoxidation processing temperature is applied to the sintering body surface except this external electrode paste application section. The manufacture method of the grain-boundary insulation type laminating ceramic condenser according to claim 1 which is characterized by performing reoxidation processing of a sintered compact and printing diffusion process of the glass to a sintered compact simultaneously with printing of the aforementioned external electrode.

[Claim 3] External electrode paste is applied to the ends side of the sintered compact which the drawer section of an internal electrode exposed so that it may connect with the above-mentioned internal electrode electrically. After performing reoxidation processing of a sintered compact simultaneously with printing of an external electrode, the glass paste which has the melting point lower than the above-mentioned reoxidation processing temperature is applied to the sintering body surface except the aforementioned external electrode formation section. The manufacture method of the grain-boundary insulation type laminating ceramic condenser according to claim 1 characterized by performing printing diffusion process of glass.

[Claim 4] The manufacture method of the grain-boundary insulation type laminating ceramic condenser any one publication of the claim 1-3 characterized by applying the glass paste produced using the end of a glass powder whose particle size is 0.1-0.5 micrometers by composition of glass consisting of Li2 O-Na2 O-SiO2 or BaO-Na2 O-SiO2.

[Translation done.]

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-340090**
(43)Date of publication of application : **10.12.1999**

(51)Int.Cl. **H01G 4/30**

(21)Application number : **10-148970**
(22)Date of filing : **29.05.1998**

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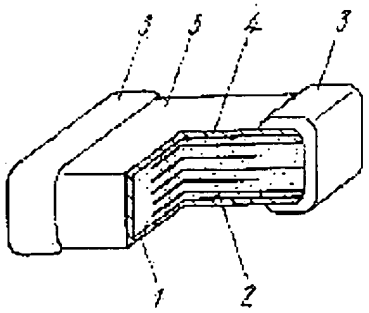
(54) MANUFACTURE OF GRAIN BOUNDARY INSULATED MULTILAYER CERAMIC CAPACITOR

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a grain boundary insulated multilayer ceramic capacitor exhibiting a high moisture resistance.
SOLUTION: The surface of a sintered compact of grain boundary insulating type multilayer ceramic capacitor containing strontium and barium titanate as major component is coated with glass paste exhibiting a lower melting point than the reoxidation temperature of the sintered compact. Then baking and diffusion is performed to form a glass diffused layer 4 on the surface of the sintered compact. In this way, many pores in the surface part of the sintered compact are filled with glass through the baking and diffusion of glass in order to prevent the moisture from penetrating to the inside of the sintered compact even in a high humidity atmosphere and to prevent degradation of characteristics.



LEGAL STATUS

[Date of request for examination] 11.05.2001

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of a grain-boundary insulation type laminating ceramic condenser (a multilayer capacitor is called henceforth).
[0002]
[Description of the Prior Art] The conventional multilayer capacitor is shown in drawing 2 . For 31, as for an internal electrode and 33, in drawing, a dielectric layer and 32 are [an external electrode and 35] overcoat films.
[0003] First, a green sheet is produced for the slurry which added and produced the binder, the plasticizer, etc. to the ceramic-dielectric powder which makes strontium-titanate barium a principal component using a doctor blade method.
[0004] Next, the paste for internal electrodes 32 which makes palladium a principal component is printed on the front face of the produced green sheet. Then, two or more sheet laminating pressurization of the green sheet which applied the paste for internal electrodes 32 is carried out, and a layered product is produced. Under the present circumstances, the drawer section of an internal electrode 32 carries out the laminating so that it may expose to the edge where a layered product conflicts on both sides of a dielectric layer 31. After cutting this layered product in a predetermined configuration, it calcinates in predetermined temperature and predetermined atmosphere, and a sintered compact is obtained.
[0005] Subsequently, after applying the paste for the external electrodes 33 which makes silver a principal component so that it may connect with the drawer section of the internal electrode 32 exposed to the ends side of this sintered compact electrically, reoxidation processing of a sintered compact was performed with printing of the external electrode 33 in predetermined temperature and predetermined atmosphere, and the multilayer capacitor was produced.
[0006] And the alkoxide etc. was used for the front face of the sintered compact except the formation section of the external electrode 33, and the overcoat film 35 was formed in it.
[0007]
[Problem(s) to be Solved by the Invention] However, the multilayer capacitor which makes a principal component the above-mentioned conventional strontium-titanate barium system ceramic dielectric Since a degree of sintering was low and much pore existed in the sintering inside-of-the-body section, although there is a trouble that property degradation will arise in " moisture-proof load life test and the overcoat film was prepared in the sintering body surface of a multilayer capacitor with various material, such as an alkoxide, as this cure The technical problem that property degradation could not fully be prevented occurred.
[0008] this invention cancels this trouble, and is equal to the prolonged use in high humidity atmosphere, and it aims at offering a multilayer capacitor with the high reliability which property degradation does not produce.
[0009]
[Means for Solving the Problem] It prevents filling up with glass much pore which exists in the surface section of a sintered compact by applying the glass paste which has the low melting point from reoxidation processing temperature, and performing printing diffusion process of glass into the sintering body surface of the multilayer capacitor to which this invention makes strontium-titanate barium a principal component, and moisture entering into it to the sintering inside-of-the-body section also in high humidity atmosphere, in order to solve the above-mentioned technical problem, and property degradation is prevented.
[0010]
[Embodiments of the Invention] The dielectric layer to which invention of this invention according to claim 1 makes strontium-titanate barium a principal component, The glass paste which has the low melting point from the reoxidation processing temperature of this sintered compact is applied to the sintering body surface of the layered product which carried out two or more layer laminating of the internal electrode by turns. What applied the glass paste which is the manufacture method of the multilayer capacitor characterized by performing printing diffusion process, and has the low melting point from sintered-compact reoxidation temperature in a sintering body surface by carrying out printing diffusion process The applied glass paste can fuse by the stoving temperature, can be spread in the sintering inside-of-the-body section through the grain boundary of a sintered compact, and pore, and can protect between sintered-compact particles with glass, osmosis in the sintering inside-of-the-body section of humidity can be prevented as this result, and, thereby, degradation prevention of a sintered-compact property can be aimed at.
[0011] Invention of this invention according to claim 2 to the sintered-compact ends side which the internal-electrode drawer

section exposed After applying external electrode paste so that it may connect with an internal electrode electrically, The glass paste which has the low melting point from the reoxidation processing temperature of the aforementioned sintered compact is applied to the sintering body surface except this external electrode paste application section. It is the manufacture method of the multilayer capacitor according to claim 1 which is characterized by performing printing diffusion process of glass to reoxidation of a sintered compact, and a sintered compact simultaneously with printing of the aforementioned external electrode paste. Simultaneously with printing of the applied external electrode paste, the applied glass paste by performing diffusion process to a sintered compact A fluidity can increase more, and the glass composition which has the low melting point from the stoving temperature of an external electrode can make the sintering inside-of-the-body section able to diffuse glass uniformly, and can raise the moisture resistance of a sintered compact.

[0012] Invention of this invention according to claim 3 to the sintered-compact ends side which the internal-electrode drawer section exposed After applying external electrode paste and performing reoxidation processing of a sintered compact simultaneously with external electrode printing, The glass paste which has the low melting point from the reoxidation processing temperature of this sintered compact is applied to the sintering body surface except the aforementioned external electrode formation section. It is the manufacture method of the multilayer capacitor according to claim 1 characterized by performing printing diffusion process of glass. Moisture resistance can be raised without affecting the property of the reoxidated sintered compact, in order to apply a glass paste to the sintered compact which reoxidation processing of external electrode printing and a sintered compact finished and to perform diffusion process of glass at low temperature from an external electrode stoving temperature.

[0013] Glass composition consists of Li2 O-Na2 O-SiO2 or BaO-Na2 O-SiO2, and it is the manufacture method of the multilayer capacitor any one publication of a claim 1 to the claim 3 characterized by using the powder of glass with a particle size of 0.1-0.5 micrometers, and invention of this invention according to claim 4 is lower than an external electrode stoving temperature, and shows the permeability which was moreover excellent to the sintered compact.

[0014] 1 operation gestalt of this invention is explained below.

(Gestalt 1 of operation) For a layered product and 2, as for an external electrode and 4, in drawing 1 , an internal electrode and 3 are [1 / a glass diffusion layer and 5] overcoat films.

[0015] First, after having made weighing capacity of the silicon oxide 3wt% and oxidization aluminum 2wt% barium-titanate 15wt% yttrium-oxide 5wt% niobium-oxide 10wt% of the accessory constituent, adding pure water and mixing with a ball mill strontium-titanate 65wt% of a principal component for 24 hours, dryness was performed and the charge of an admixture was produced.

[0016] Next, after performing temporary quenching for the charge of an admixture at the temperature of 1100 degrees C for 2 hours, pure water was added to temporary-quenching material, and it ground for 17 hours, and it dried after that, and dielectric materials were obtained.

[0017] Then, a binder, a plasticizer, and the organic solvent are added to dielectric materials, and after kneading for 24 hours and considering as a slurry, a green sheet with a thickness of 30 micrometers is produced using a doctor blade method.

[0018] The paste for internal electrodes 2 which makes palladium a principal component is printed to the produced green-sheet side. Then, the 30-sheet laminating of the green sheet which printed the paste for internal electrodes 2 is carried out using the well-known laminating ceramic condenser manufacture method, and a layered product is produced.

[0019] The produced layered product is cut in a predetermined multilayer-capacitor configuration, and it degreases at the temperature of 1100 degrees C among [after forming a layered product 1] the atmosphere, and succeedingly, baking is performed at the temperature of 1300 degrees C among the green gas atmosphere of 10% of hydrogen for 2 hours, and a sintered compact is produced.

[0020] Next, reoxidation processing of a sintered compact is carried out for the paste for the external electrodes 3 which makes silver a principal component to the ends side of the sintered compact to which barrel finishing of a sintered compact was performed and the internal electrode 2 was exposed with printing of the external electrode 3 at the temperature of 850 degrees C after an application and dryness and among the atmosphere for 1 hour.

[0021] Subsequently, after applying the low-melting-glass paste of 650 degrees C of melting points which make a principal component Li2 O:Na2 O:SiO 2= 10:20:70 which ground the pitch diameter to 0.3 micrometers to the front face except the external electrode 3 formation section of the sintered compact which was able to be printed in the external electrode 3, heat treatment is performed on it for 5 minutes at the temperature of 800 degrees C among the atmosphere, and the glass diffusion layer 4 is formed in it at a sintered compact.

[0022] Then, barrel finishing of the sintered compact was carried out again, after removing the glass component adhering to external electrode 3 front face, overcoat film 5 processing was performed to the sintering body surface except the external electrode 3 formation section, and the multilayer capacitor was produced.

[0023] The obtained multilayer capacitor (A) and the multilayer capacitor which omits overcoat film 5 processing after forming the glass diffusion layer 4 (B), and the conventional example (C) (what performed only overcoat film 5 processing to the sintering body surface after the external electrode 3 was able to be printed) -- about each sample constant temperature (85 degrees C and 85Rh%) -- moisture-proof life test held to a constant humidity chamber for 1000 hours -- carrying out -- the electrostatic capacity before and behind a humidity resistance test, and the rate of change of voltage at reference current -- moreover, the migration situation of the silver of the external electrode 3 was investigated, and the result was shown in (Table 1)

[0024]

[Table 1]

	耐湿寿命試験特性変化率		
	静電容量	バリスタ特性	マイグレーション
(A)	− 0.1%	−0.02%	認められず
(B)	− 0.1%	−0.01%	認められず
(C)	− 1.2%	−11.2%	若干認められる
(D)	−95.0%	−92.0%	認められる

[0025] As shown in (Table 1), the rate of change of electrostatic capacity and voltage at reference current of the thing (A) in which the glass diffusion layer 4 of the low melting point of this invention was formed is very small, and, moreover, silver migration is not accepted. Moreover, what performed overcoat film 5 processing to the sintering body surface which established the glass diffusion layer 4 of the low melting point (B) can make small further the rate of change of voltage at reference current. On the other hand, what performed only overcoat film 5 processing to the sintered compact (C) had the large rate of change of electrostatic capacity and voltage at reference current, and, moreover, silver migration was accepted in some products. What furthermore omits glass diffusion layer 4 processing and overcoat film 5 processing (D) has still larger rate of change, and migration has generated it between the internal electrodes 2 of a sintered compact, and between the external electrodes 3.
[0026] As shown in drawing 1 , while the low melting glass of applied Li2 O-Na2 O-SiO2 formed the glass diffusion layer 4 in the surface section of a sintered compact from this result, as a result of being spread in a sintered-compact grain boundary and filling an internal pore portion, resistance to humidity improves and it is thought that change of an electrical property was mitigated. Moreover, in order to check this, as a result of grinding this invention article and observing a sintered compact, the glass diffusion layer 4 of about 200-micrometer thickness was accepted in the sintering body surface layer, and having filled up with glass in the internal pore of the surface section was admitted.
[0027] In addition, about low-melting-glass powder, if what has a particle size smaller than 0.1 micrometers is used, production of a paste will become difficult from a viscous limitation at the time of kneading with a binder and a solvent. Moreover, if a larger thing than 0.5 micrometers is used, since the fluidity of glass will fall at the time of 800-degree C heat treatment and it will be hard coming to carry out diffusion to the sintering inside-of-the-body section, it is not desirable. Furthermore, although low-melting-glass processing was performed after printing of the external electrode 3 in this operation gestalt, even if it performs glass processing simultaneously with printing of the external electrode 3, it is also checked that the same result is obtained. Overcoat film 5 processing is for preventing the waterdrop which formed the water-repellent layer in the sintering body surface, and dewed the multilayer-capacitor front face permeating the sintering inside-of-the-body section.
[0028] (Gestalt 2 of operation)
Perform (the gestalt 1 of operation), and barrel finishing of the sintered compact produced on these conditions, and the paste for external electrode 3 which makes silver a principal component is applied to the ends side of the sintered compact which exposed the internal electrode 2 to the end face. After reoxidating a sintered compact simultaneously with printing of the external electrode 3 at the temperature of 850 degrees C among the atmosphere for 1 hour, The low-melting-glass paste of 690 degrees C of melting points which make a principal component BaO:Na2 O:SiO 2= 10:5:85 (wt%) which ground the external electrode 3 to the sintering body surface which was able to be printed at 0.3 micrometers of pitch diameters is applied. Heat treatment is performed for 5 minutes at the temperature of 800 degrees C among the atmosphere, and the glass diffusion layer 4 is formed in a sintered compact.
[0029] Then, barrel finishing of a sintered compact was performed, after removing the glass component adhering to external electrode 3 front face, overcoat film 5 processing was performed to the sintering body surface except the external electrode 3 formation section, and the multilayer capacitor was produced.
[0030] The obtained multilayer capacitor (E) and the multilayer capacitor which omits overcoat film 5 processing after forming the glass diffusion layer 4 (F), And the thing which performed only overcoat film 5 processing to the sintering body surface after the external electrode 3 was able to be printed as a conventional example (G), each sample (gestalt 1 of operation) -- moisture-proof life test of these conditions -- carrying out -- the electrostatic capacity before and behind a humidity resistance test, and the rate of change of voltage at reference current -- moreover, the migration situation of the silver of the external electrode 3 was investigated, and the result was shown in (Table 2)
[0031]
[Table 2]

	耐湿寿命試験特性変化率		
	静電容量	バリスタ特性	マイグレーション
(E)	− 3.2%	− 5.3%	若干認められる
(F)	− 0.5%	− 0.3%	認められず
(G)	− 1.2%	−11.2%	若干認められる
(H)	−95.0%	−92.0%	認められる

[0032] As shown in (Table 2), the thing (E) in which the BaO-Na2 O-SiO2 glass diffusion layer 4 of this operation form was formed, from the case of Li2 O-Na2 O-SiO2 glass Electrostatic capacity, Although the rate of change of voltage at reference current is a little large, a bird clapper turns out that utilization is fully possible conventionally in elegance (thing (F which performs overcoat film 5 processing to the sintering body surface which was very small compared with G) and formed the glass diffusion layer 4).

[0033] As BaO-Na2 O-SiO2 applied glass was shown in drawing 1 like (the operation form 1), while forming the glass diffusion layer 4 in the surface section of a sintered compact from this result, as a result of being spread in a sintered-compact grain boundary and filling an internal pore portion, resistance to humidity improves and it is thought that change of an electrical property mitigated. Moreover, in order to check this, as a result of grinding this invention article and observing a sintered compact, the glass diffusion layer 4 was accepted in the sintering body surface layer, and having filled up with glass in the pore of the sintering inside-of-the-body section was admitted.

[0034] While making a sintering body surface layer precise from the above result by forming the glass diffusion layer 4 of the melting point lower than the stoving temperature of the external electrode 3 in the strontium-titanate system multilayer-capacitor sintered compact which is inferior in a degree of sintering, it can fill up with the glass which diffused internal pore, the reliable multilayer capacitor excellent in resistance to humidity can be offered, and it turns out that utility value is industrially high. Moreover, it is for considering so that the glass with which performing printing diffusion process fused the glass which has the melting point lower than the stoving temperature of the external electrode 3 by the stoving temperature may increase a fluidity and it may fully be spread in the sintering inside-of-the-body section. In addition (Table 2), although (H) has formed neither the glass diffusion layer 4 nor the overcoat film 5, it is a property.

[0035]

[Effect of the Invention] By applying and carrying out printing diffusion process of the glass which has the melting point lower than the stoving temperature of the external electrode which forms a strontium titanate in the edge of the sintered compact of the multilayer capacitor made into a principal component above according to this invention, the surface of a sintered compact can be turned precisely, it can fill up with the glass which diffused the pore of the sintering inside-of-the-body section, and the reliable multilayer capacitor which was excellent in moisture resistance with this can be offered.

[Translation done.]